

ARMY RESEARCH LABORATORY

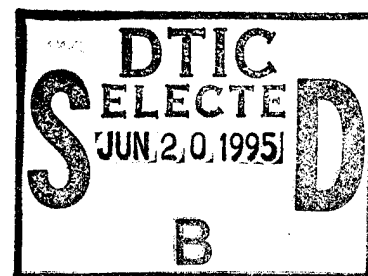


Spectral Analysis for Rare-Earth Ions in Transparent Solids

by Clyde A. Morrison and Donald E. Wortman

ARL-TR-635

June 1995



19950619 092

DTIC QUALITY INSPECTED 3

Approved for public release; distribution unlimited.

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE June 1995		3. REPORT TYPE AND DATES COVERED Final, from FY94
4. TITLE AND SUBTITLE Spectral Analysis for Rare-Earth Ions in Transparent Solids			5. FUNDING NUMBERS PE: H44	
6. AUTHOR(S) Clyde A. Morrison and Donald E. Wortman				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory Attn: AMSRL-PS-AA 2800 Powder Mill Road Adelphi, MD 20783-1197			8. PERFORMING ORGANIZATION REPORT NUMBER ARL-TR-635	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Laboratory 2800 Powder Mill Road Adelphi, MD 20783-1197			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES AMS code: P611102.H44 ARL PR: 4R7A71				
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A model was developed that includes a crystal-field Hamiltonian and the free-ion Hamiltonian for the analysis of the spectra of rare-earth ions in transparent solids. The report discusses phenomenological crystal-field parameters, B_{km} , obtained by the fitting of the experimental data of a particular ion-host combination, as well as their relationship with the derived crystal field parameters. The latter parameters, the derived B_{km} , and factors affecting the Hartree-Fock values of $\langle r^k \rangle$, such as shielding, wave function expansion, etc, are considered in detail. The theory of the transition probabilities of electric and magnetic dipole transitions are presented, as well as magnetic g factors, line strengths, branching ratios, and lifetimes. The entire work leans heavily on the investigations, both theoretical and experimental, performed at Harry Diamond Laboratories (now part of the Army Research Laboratory), and this work is referenced throughout this report.				
14. SUBJECT TERMS Rare-earth spectra, lasers, triply ionized rare-earth ions			15. NUMBER OF PAGES 31	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	

Preface

New lasers that are more efficient and operate at other wavelengths than those currently in use are constantly being required for a variety of purposes. In addition to commercial uses, military uses vary, for example, from communications, range finding, missile guidance, and countermeasures to high-powered weapons systems and nuclear fusion. The development of lasers with new, unique properties is desirable also because they stimulate new commercial and military uses that previously may have been unforeseen.

Solid-state laser materials doped, primarily, with triply ionized lanthanides (rare-earth ions) play an important role in this scheme. New varieties of exotic single-crystal materials are continuing to be developed, and it is desirable to have a method for predicting their potential properties as laser host materials. New lanthanide/host laser systems generally must rely on time-consuming and costly experimental programs for evaluation of their efficiency. The effort required also is very massive for developing techniques to grow optical quality crystals of sufficiently large dimensions.

There is a need, therefore, to have a theoretical capability to aid in the selection, from among the many lanthanide/host combinations, of the systems that offer the best potential for fulfilling a predetermined set of requirements. The theoretical effort in the area of laser research at the Army Research Laboratory has been directed toward this goal. In this effort, we developed a consistent model of the host and interactions to predict spectra and intensities for all the lanthanides in a given host and predict these quantities for new systems.

Accession For	
DTIC GRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Dist	Avail and/or Special

Contents

Preface	3
1. Introduction	7
2. Background	8
2.1 Phenomenological B_{km}	8
2.2 Derived B_{km}	10
2.3 Electric and Magnetic Dipole Transition Probabilities and Branching Ratios	11
3. Computer Programs	13
4. Analysis of Rare-Earth Spectra	14
5. Conclusion	17
Acknowledgments	18
References	19
Distribution	27

1. Introduction

Solid-state laser materials, for the most part, involve a triply ionized lanthanide (rare-earth ion) as a dilute substitutional impurity in a crystalline host material. There are exceptions, such as the lanthanide pentaphosphates ($\text{LnP}_5\text{O}_{14}$) that, rather than being dilute, are effectively 100-percent doped, and the glasses that are not crystalline in the sense of a systematic lattice. However, in the pentaphosphates very little concentration quenching is observed, indicating that each lanthanide ion is electronically isolated, and in the glasses some local ordering exists near the impurity so that, in either case, one may consider the effects in the context of the original assumptions.

The 13 interesting triply ionized lanthanides from Ce^{3+} through Yb^{3+} have complete electronic inner cores through the $4d^{10}$ shell and outer shells of $4f^N 5s^2 5p^6$, where $1 \leq N \leq 13$. The incomplete $4f$ shell is optically active. It has a multitude of energy levels (representing the many ways N individual electrons may orient their angular momenta with respect to each other), between which the ion may make transitions and release or absorb radiation. These energy levels are highly degenerate in the free ion, but in the presence of the electrostatic (crystal) field due to the constituent ions of the host material, a splitting occurs that manifests the breakdown of spherical symmetry in crystals. The outer $5s^2 5p^6$ electrons, as well as the inner core to a lesser extent, serve to shield this crystal field, so that in contrast with the transition-metal ions, the crystal field can be considered quite accurately as a perturbation on the free ion.

The methods of our theoretical study of this problem are as follows:

- (1) To obtain free-ion wavefunction bases for the $4f^N$ configurations to be used in calculating interactions relevant to the triply ionized lanthanides in a given host material.
- (2) To postulate a phenomenological crystal-field Hamiltonian of the form

$$H_x = \sum_{km} B_{km}^* \sum_i C_{km}(i) \quad (1)$$

having the point-group symmetry at the impurity ion site, to vary the phenomenological B_{km} in a free-ion basis of states, and to fit theoretical to experimental energy levels.

- (3) To characterize the host material so that a summation may be performed over the constituent ions to determine their cumulative electrostatic field at the impurity (lanthanide) ion site.
- (4) To consider shielding, distortion, dielectric, wavefunction overlap (covalency), and other such effects that may influence the observed spectra.

- (5) To obtain derived B_{km} from the fundamental properties of the host material (purpose 3) and other impurity-ion/host interactions (purpose 4) and to reconcile them with phenomenological B_{km} (purpose 2) by refining the characterization of the host and the nature of the interactions.
- (6) To use the resultant consistent model of the host and interactions to predict spectra and intensities for all the lanthanides in a given host, and to predict these quantities for new systems once the crystallographic parameters of a new host material are known.
- (7) To determine which systems have the greatest potential for fulfilling the requirements for a given application.

2. Background

The research concerned with identifying the energy levels of rare-earth ions in crystals and understanding the interactions that determine these Stark splittings has proceeded along two general lines. The phenomenological approach has been to diagonalize the crystal-field Hamiltonian given by equation (1) in some basis representing the f^N configuration of the particular rare earth, and to vary the B_{km} until a best fit is obtained between theoretical and experimental energy levels. The resultant B_{km} , referred to as the phenomenological crystal-field parameters, represent the net total interaction between the impurity ion and the host material and reflect the point-group symmetry at the impurity-ion site. Secondly, attempts have been made to derive the B_{km} by devising models for considering the fundamental interactions between the impurity ion and the host material. The B_{km} obtained by this method, referred to as derived crystal-field parameters, are ab initio values to be compared with the phenomenological B_{km} for testing the accuracy of models. Once the models are refined so that derived and phenomenological B_{km} are approximately equal, then the model can be used to predict the properties of new impurity-ion/host systems.

2.1 Phenomenological B_{km}

According to the discussion above, the phenomenological B_{km} that result in a best fit to experimental energy levels will not be unique, but will be functions of the basis chosen for diagonalizing H_x . Early theories employed Russell-Saunders (JLS) states and operator-equivalent techniques to obtain B_{km} that fit the experimental data in separate multiplets [1-5]. Once data were accumulated above the ground multiplets that are relatively pure, the more general operator-equivalent technique was used, which assumes (again) pure J states but with L and S mixing dependent on the free-ion Racah parameters, E^k , and the spin-orbit constant, ζ , corresponding to the Coulomb and spin-orbit interactions. In each of these procedures, J mixing by the crystal field was neglected, owing primarily to the unavailability of adequate computer facilities. Later, the entire f^2, f^3, f^{12} ,

and f^{11} configurations, respectively, of Pr^{3+} , Nd^{3+} , Tm^{3+} , and Er^{3+} were diagonalized and the B_{km} varied simultaneously with the free-ion parameters to fit observed spectra in certain host materials [6–11]. This method, while in principle the most elaborate possible, suffers from the incapability of free-ion parameters to fit observed centroids and from its inability to be extended to the other f^N configurations because of the large number of levels involved.

To circumvent some of these problems, namely tractability, lack of J -mixing, and ill-fitting of centroids, Karayianis [12] introduced the method of an effective spin-orbit Hamiltonian (ESOH). After exhaustive application [13–21], it became clear that this method too was deficient because it operated in a Russell-Saunders basis that is valid only for certain isolated multiplets.

To improve on this deficiency, Carnall et al [22] diagonalized a seven-parameter free-ion Hamiltonian, H_{FI} , of the form

$$H_{FI} = \sum_i E^k e_k + \zeta \sum_i l_i \cdot s_i + \alpha L(L+1) + \beta G(G_2) + \gamma G(R_7), \quad (2)$$

to obtain wavefunctions and reduced matrix elements. In equation (2), the E^k ($k = 1, 2$, and 3) are the Racah parameters, ζ is the spin-orbit constant, and $G(G_2)$ and $G(R_7)$ are the Casimir operators for the Lie groups G_2 and R_7 . A subspace was then chosen of several of the low-lying multiplets and their centroids (usually 10 to 12 multiplets) varied independently along with the B_{km} to fit theoretical to experimental energy levels [23]. From the resultant centroids, one may then determine the “free-ion” parameters that best fit the crystal spectra for the ion/host system in question [24]. This procedure has the advantage of complete diagonalization (provided a sufficient number of multiplets are chosen), so that the neglected multiplets do not appreciably affect the crystal splittings in the energy range of interest, and the resultant centroids do not indicate that “free-ion” parameters differ appreciably from those that initially determined the wavefunctions.

Experimental problems, as well as the theoretical one discussed above, are encountered in the process of determining phenomenological crystal-field parameters. Many spurious lines appear in the spectra, as well as the not-so-spurious ones of vibronic origin, which serve to complicate the identification process. In addition, imperfections in the host crystal as well as magnetic dipole transitions between certain levels serve to destroy the prominent electric dipole selection rules and make identification difficult. In such cases, other data are very useful, such as electron spin-resonance measurements that accurately determine the properties of the ground state [25–35]. These measurements and Zeeman measurements [36] that determine g factors for the ground and certain excited states quite frequently can be of assistance in identifying levels, as well as placing restrictions on the B_{km} , when used with the energy-level fitting procedure [37]. The partial g -sum rule has been developed in this connection to provide experimentalists with a further tool for identifying spectra [38].

2.2 Derived B_{km}

The approach to deriving crystal-field parameters begins with the ligand field assumption that gives

$$B_{km} = \langle r^k \rangle A_{km} , \quad (3)$$

where $\langle r^k \rangle$ is the k th moment of the impurity ion's radial wavefunction and the A_{km} are components of the spherical tensor decomposition of the crystalline electrostatic field, referred to as crystal-field components. To evaluate the A_{km} , one begins with a simple point-charge lattice sum [34,39,40]. Other refinements have been included, such as the effects of higher moments of charge distribution of neighboring ions [41,42], overlap with the ligand [43–45], and molecular orbitals involving the rare-earth ion [46]. The most significant modification to equation (3) was a result of considering the shielding effects of the outer $5s^2 5p^6$ and the inner core electrons that are expressed in the form of shielding factors [47–51], σ_k , which gives

$$B_{km} = \langle r^k \rangle (1 - \sigma_k) A_{km} . \quad (4)$$

Other effects, notably possible local distortion of the crystalline host material, that could revise the form of derived B_{km} or affect the results in other ways were investigated and discarded [52], with the exception of a modification of $\langle r^k \rangle_{\text{HF}}$ evaluated with Hartree-Fock (HF) radial wavefunctions [53–56]. Since calculations of Slater integrals using HF wavefunctions give very much larger values than those determined experimentally [57,58], it was concluded that an appropriate modification to the HF values of $\langle r^k \rangle$ should be

$$\langle r^k \rangle = \tau^{-k} \langle r^k \rangle_{\text{HF}} , \quad (5)$$

where $\tau < 1$. The τ for each lanthanide are assumed to be approximately host-independent, consistent with previous calculations that show Slater integrals to be only moderately host-dependent [59,60]. Other improvements in the techniques for evaluating $\langle r^k \rangle$ that have not yet been incorporated in these calculations include electron correlation effects [61] (that correspond to higher order corrections to the many-body problem), relativistic effects [62], and the dielectric effects of the medium [60]. We have obtained values for the A_{km} for a number of hosts by performing a lattice sum assuming valence charges for the constituent ions of the host lattice [63]. Brewer [64] later incorporated covalency effects, known to be important for tightly bound radicals in the lattice, by assuming an arbitrary charge q for the covalent anion, consistent with the total charge of the radical, and considering its effective position, η , to be slightly shifted from the nuclear position. The $A_{km}(q\eta)$ obtained in this manner are functions of the q and η , which were then varied along with τ defined above to fit derived $B_{km}(\tau; q\eta)$ of the form

$$B_{km}(\tau; q\eta) = \tau^{-k} \langle r^k \rangle_{\text{HF}} (1 - \sigma_k) A_{km}(q\eta) \quad (6)$$

to phenomenological B_{km} determined by the ESOH method for several lanthanides in CaWO_4 [65].

Later, improvements on the method for determining the A_{km} were developed by the self-consistent inclusion of the electrostatic field due to electric dipoles induced in the host lattice [66]. This, in effect, obviates the use of the fictitious η and replaces it with other parameters, the polarizabilities of the host ions. The inclusion of the host's dipoles may result in a more accurate representation of the host, as well as in the parameterization of the electrostatic field in terms of measurable quantities such as the polarizabilities.

2.3 Electric and Magnetic Dipole Transition Probabilities and Branching Ratios

The odd- k A_{km} , the r^k expectation values between the lower $4f$ and higher nd and ng configurations, and $\Delta_{nl} = E_{nl} - E_{4f}$ energy differences [64,67] are required for calculating electric dipole intensities for the lanthanides [68–70]. Recent methods for obtaining some of the $\langle nl || r^k || 4f \rangle$ and Δ_{nl} have given fairly accurate results for these quantities in the Hartree-Fock approximation, and interpolations have given approximate values for all the lanthanides [71]. Crystal wavefunctions that result from the fitting of energy levels with a phenomenological Hamiltonian are used to obtain level-to-level intensities for various polarizations to be compared with experiment [72]. These calculations provide a crucial test for the adequacy of the models. A fairly complete set of predicted spectra and intensities assuming S_4 or higher point-group symmetry has been reported for all the lanthanides in 10 host materials [73–82]: CaWO_4 , LiYF_4 (yttrium lithium fluoride—YLF), YVO_4 , YPO_4 , YAsO_4 , $\text{Y}_2\text{SiBe}_2\text{O}_7$, $\text{Y}_3\text{Al}_5\text{O}_{12}$ (yttrium aluminum garnet—YAG), $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (yttrium gallium garnet—YGG), YAlO_3 (YALO), and $\text{LnP}_5\text{O}_{14}$ where Ln is one of the lanthanides.

In the intensity calculations for rare-earth ions, as in cases [83] like LaF_3 , the dipole operator, $\mathbf{p} = -e\mathbf{r}$, is replaced by the effective dipole operator of Judd [68] and Ofelt [69] by

$$\mu_\alpha = -\sqrt{\frac{7}{3}} \sum_{k,t} (2t+1) N_k(t) (A^{(k)} U^{(t)})_\alpha^{(1)}, \quad (7)$$

where $\alpha = 0, \pm 1$, $t = 2, 4$, and 6 , and $k = 1, 3, 5$, and 7 , with $(A^{(k)} U^{(t)})_\alpha^{(1)}$ representing a coupling of the irreducible tensors $A^{(k)}$ and $U^{(t)}$ by a Clebsch-Gordan coefficient to form a tensor of rank 1 and projection α . The $A^{(k)}$ is a tensor whose components are A_{km} . In equation (7), a factor e , the electronic charge, has been suppressed so that the units of μ are angstroms and those of S_{if} (to be discussed later) are \AA^2 . Also,

$$N_k(t) = \sum_l \sqrt{2l+1} W(k133;t l) R_k(t) \langle l(0) 1(0) | 3(0) \rangle \langle 3(0) k(0) | l(0) \rangle, \quad (8)$$

where the sum covers the values $l = 2$ and 4 , $W(abcd;ef)$ is a Racah coefficient, and $\langle a(\alpha) b(\beta) | c(\delta) \rangle$ is a Clebsch-Gordan coefficient [84]. The $R_k(l)$ of equation (8) are given by

$$R_k(l) = \sum_n \langle 4f | r^k | nl \rangle \langle nl | r | 4f \rangle / \Delta E_{nl} , \quad (9)$$

where $\langle n'l' | r^k | nl \rangle$ are radial matrix elements of r^k between states nl and $n'l'$ and ΔE_{nl} is the difference [85] in energy between the configurations $4f^{N-1}nl$ or $3d^9 4f^{N+1}$ and the configuration $4f^N$. Values of $R_k(l)$ for all the triply ionized rare-earth ions are given elsewhere (Leavitt and Morrison [83], table II) along with the detailed description of the derivation of the results. The electric dipole line strengths were computed from

$$S_{fi}^e = \sum_{f,i} |\langle f | r | i \rangle|^2 \quad (10)$$

where the sum on f and i on the right side covers the various components of the wave functions of the energy levels of f and i .

The magnetic dipole operator used in the computations is

$$\mathbf{M} = \frac{1}{2} \alpha_0 a_0 (\mathbf{L} + g_e \mathbf{S}) , \quad (11)$$

where α_0 is the fine structure constant and a_0 is the Bohr radius. Also, as in the case of the electric dipole operator, the electronic charge is suppressed and g_e is the free-electron g -factor. Similar to equation (10), the magnetic dipole line strength is

$$S_{fi}^m = \sum_{f,i} |\langle f | m | i \rangle|^2 . \quad (12)$$

In both the electric and magnetic dipole cases, a multiplet-to-multiplet line strength is defined by

$$S_{JJ'} = \sum_{if} S_{fi} ,$$

where i refers to the levels in the multiplet J and f refers to the levels in J' . The multiplet-to-multiplet branching ratios for electric or magnetic dipole transitions are given by

$$\beta_{JJ'} = \frac{(E_J - E_{J'})^3 S_{JJ'}}{\sum_{JJ'} (E_J - E_{J'})^3 S_{JJ'}} , \quad (13)$$

with the J' sum covering all multiplets such that $E_J > E_{J'}$, and we have assumed that each multiplet is equally populated. All the above quantities and some combinations were calculated elsewhere [83] as well as g values, where they exist, for each level. The comparison with experimental results was, in general, very good and gave considerable confidence in the method and encouragement toward future computations.

3. Computer Programs

Computer programs were developed at Harry Diamond Laboratories (now part of the Army Research Laboratory) to perform the calculations required in the above work. These programs were then extended so that we can now perform the following calculations for all the lanthanides, $4f^N$, and actinides, $5f^N$, for $1 \leq N \leq 13$:

- (1) Calculate free-ion energies and derivatives with respect to the seven free-ion parameters, $E^1, E^2, E^3, \zeta, \alpha, \beta$, and γ .
- (2) Calculate reduced matrix elements of the unit spherical tensors $U^{(2)}, U^{(4)}$, and $U^{(6)}$ among all the free-ion wavefunctions.
- (3) Select reduced matrix elements between free-ion wavefunctions for any preassigned subspace and form crystal subspaces for any point group other than C_1 or C_i .
- (4) Diagonalize the crystal-field Hamiltonian in the subspace and vary the multiplet centroids and phenomenological crystal-field parameters to obtain a least-squares fit between theoretical and experimental energy levels.
- (5) Use centroids obtained in (4) with derivatives given in (1) to calculate new "free-ion" parameters relevant to the particular host.
- (6) Calculate electric and magnetic dipole transition probabilities between all crystal levels for any point group other than C_1 or C_i .

For deriving crystal-field parameters, a general lattice sum program has been developed for any site in the 230 space groups that can determine the electrostatic field due to the monopoles of the host ions — represented by A_{km}^M — and the self-consistent dipole — represented by A_{km}^D .

Programs have also been written to perform a variety of less complicated calculations, such as determining branching ratios for the fluorescence of a higher multiplet to lower multiplets for any rare earth in any host material. We can then compare these multiplet-to-multiplet transition probabilities with sums over individual level-to-level transition probabilities to establish the effects of multiplet mixing by the crystal field. Also, the Judd-Ofelt parameters, Ω_k , are calculated along with the g -factors where applicable to the particular ion/host combination.

The first application of all the computations mentioned above was to the analysis of a number of rare-earth ions in LaF_3 . In this host, which is hex-

agonal, the rare-earth ions occupy sites with C_2 symmetry, with the principal C_2 axis perpendicular to the c -axis of the crystal. This calculation of all quantities was therefore a stringent test of the theory as developed above. In addition, other programs have been written to evaluate the laser properties, such as threshold conditions, slope efficiency, etc, of single and two-species lasers as functions of the transition probabilities calculated as described in (6).

4. Analysis of Rare-Earth Spectra

The analysis of the spectra of rare-earth ions [86] in LaF_3 is presented in some detail since the method used in the analysis is, in general, the same as used presently for those hosts where the rare-earth ion is assumed to occupy a site of low symmetry (C_2 , C_s , D_2 , C_{2h} , and a crude approximation to C_1 or C_i).

The methods outlined in section 2 were used in the analysis of the experimental data taken on a number of rare-earth ions in the host materials given in that section. That is, values of $\rho_k = \langle r^k \rangle_{HF} (1 - \sigma_k) / \tau^k$ for each of the rare-earth ions were found, and they are given elsewhere [86]. These ρ_k were used to determine $B_{km} = \rho_k A_{km}$, with the A_{km} obtained by the monopole terms only and the latest detailed x-ray results for LaF_3 . The B_{km} were then used as starting values in each ion with an odd number of electrons for which experimental data existed, and we determined a best fit to the experimental data by varying the B_{km} . The ions with an odd number of electrons were chosen because in C_2 symmetry there is essentially only one type of Kramer's doublet with the irreducible representation $\Gamma_{3,4}$ for these ions. We divided the B_{km} thus determined by ρ_k to determine a phenomenological set of A_{km} ; since it is assumed that the A_{km} are functions of the host only and not ion dependent, we simply averaged the set of A_{km} to obtain a unique A_{km} for each allowed value of k and m . These A_{km} were then used again as starting values in the fitting procedure, with possibly some reassignment of levels, and the fitting process repeated until it was determined that nothing more could be gained by continuing the process. The resulting A_{km} were then used as starting values in the same fitting process of the data on ions with an even number of electrons. Finally, the same procedure was used on all the ions employing all the experimental data.

A similar, but more extensive, analysis was made on rare-earth spectra and intensity measurements of these ions doped in Y_2O_3 [85,87-90]. This host material has two types of sites; one site has C_2 symmetry and the other site has C_{3i} symmetry. The latter site has much weaker absorption, as only magnetic dipole transitions are allowed in C_{3i} symmetry. The agreement between experiment and theory for the C_{3i} site was quite poor. The agreement with experiment was better on the C_2 sites, but not as good as was achieved for the calculations on rare-earth ions in LaF_3 . A similar calculation to the above was done on the spectra of Nd^{3+} and Er^{3+} in

$\text{Bi}_4\text{Ge}_3\text{O}_{12}$ [91], but most of the calculation was of a predictive nature because of a lack of experimental data on rare-earth ions in this host.

The absorption spectra of a number of rare-earth ions in $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) [92–96] have been analyzed with phenomenological crystal-field parameters obtained in all cases, but with only limited application of the other aspects of the theory described above. The analysis was limited to comparison with available experimental data.

Similarly, the absorption and emission spectra of a number of rare-earth ions in mixed garnets [97–101] have been analyzed with phenomenological crystal-field parameters obtained and branching ratios calculated in many cases. One result obtained for all the garnets analyzed was that the best fit to the phenomenological B_{km} was achieved with an oxygen charge, $q_0 = -1.8$, which is used in the monopole sum given by

$$A_{km} = -e^2 \sum_j \frac{q_j C_{km}(\hat{R}_j)}{R_j^{k+1}}, \quad (14)$$

where q_j is the charge (in units of electronic charge) on the ion at \mathbf{R}_j .

A different application of the theory was in the analysis of the spectra of triply ionized erbium in ErAs [102]. The absorption spectra of Er^{3+} in a thin film of ErAs, which was grown by molecular beam epitaxy on a substrate of GaAs, were reported [103]. In ErAs the erbium ion site has O_h symmetry, and only magnetic dipole transitions are allowed. The reported energy levels were analyzed, and the phenomenological crystal-field parameters, B_{km} , were obtained. These B_{km} and the matrix elements of the magnetic dipole operator were used in equation (12) to give the calculated absorption spectra as a function of temperature. A Lorentz line shape was assumed with a line width of 3 cm^{-1} as reported, and when the results were plotted on a comparable scale, practically a perfect match was achieved for the three temperatures of the reported data. Later the analysis was extended [104] to include a prediction of the absorption spectra of other lanthanides, Ln^{3+} , in LnAs.

Recently we have been collaborating with Norman Barnes of NASA Langley Research Center and his co-workers on the analysis of potential 1.5- to 2- μm lasers. For this purpose, we chose the ions Ho^{3+} and Tm^{3+} as the lasing ions and calculated the line-to-line temperature-dependent branching ratios for these ions in the site with D_2 symmetry in 10 garnet hosts [105,106]. Of these hosts, we had good experimental data on Ho^{3+} in YAG [96] and limited experimental data on Ho^{3+} in $\text{Y}_3\text{Ga}_5\text{O}_{12}$ (YGG). Using the procedure outlined above, we found that the best fit to the phenomenological B_{km} using equation (14) was achieved for $q_0 = -1.79$. However, when we used the predicted B_{km} for Ho^{3+} in YGG, the calculated energy levels differed considerably from the experimental values. We then decided to obtain a better set of ρ_k for Ho^{3+} by using the concept of rotational invariance [107–109]; that is,

$$\rho_k = S_k(B)/S_k(A) , \quad (15)$$

where

$$S_k(X) = \left[\sum_{m=-k}^k X_{km}^* X_{km} \right]^{1/2} \quad (16)$$

with $S_k(B)$ computed with the phenomenological crystal-field parameters for Ho^{3+} in YAG, and $S_k(A)$ calculated with $q_0 = -1.7$ in equation (14). With the ρ_k thus determined, the B_{km} were calculated along with the energy levels for Ho^{3+} in the remaining nine garnets. The odd- k A_{km} were also computed with equation (14) and $q_0 = -1.7$. The line-to-line radiative lifetimes were calculated for levels i in the 5I_7 multiplet to levels j in the 5I_8 multiplet of Ho^{3+} by

$$\frac{1}{\tau_{ij}} = \frac{32\pi^3\alpha_0}{3c^2} \left(X_{ij} S_{ij}^{ed} + X'_{ij} S_{ij}^{md} \right) \nu_{ij}^3 , \quad (17)$$

where

$$X_{ij} = \frac{n_{ij}(n_{ij}^2 + 2)^2}{9} , \quad (18)$$

$$X'_{ij} = n_{ij}^3 , \quad (19)$$

n_{ij} is the index of refraction at the wavelength λ_{ij} ($\lambda_{ij}(\mu\text{m}) = 10^4/(E_i - E_j)$) and α_0 is the fine structure constant ($1/\alpha_0 = 137.0373$).

The branching ratios as a function of temperature are given by

$$\beta_{ij}(T) = \frac{\frac{Z_i}{\tau_{ij}}}{\sum_{ij} \frac{Z_i}{\tau_{ij}}} \quad (20)$$

and

$$Z_i = \frac{e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} . \quad (21)$$

In equations (17) through (21), it is assumed that i belongs with levels in the 5I_7 multiplet and j belongs with levels in the 5I_8 multiplet. The temperature-dependent branching ratios were calculated with equation (20). Equations (17) through (21) above were also used in a model of a quasi four-level laser, and it was found that for room temperature, the $Y_3Ga_5O_{12}$ (YGG) host had the lowest threshold for $^4I_7 \rightarrow ^4I_8$ laser threshold.

These computations were repeated for Tm^{3+} in the 10 garnets with the transition from the 3F_4 to the 3H_6 multiplet (the 4F_4 multiplet is frequently labeled the 3H_4 multiplet). In the calculations for both Ho^{3+} and Tm^{3+} , the index of refraction in each garnet was represented by a Sellmeier equation with the constants in the equation determined by fitting of the experimental values. In most analyses of data taken on the spectra of the heavy rare-earth ions in the garnet hosts, the transitions are assumed to be electric dipole, and the Judd-Ofelt parameters, Ω_k , are used. However, because of the strong crystal fields in the garnets, there is considerable J mixing in the wavefunctions that is not taken into account by the simple Judd-Ofelt analysis, which assumes electric dipoles only and no J mixing by the crystal field [110]. Further, we have found that for many of the transitions, the strength of the magnetic dipole given by equation (12) was as large or larger than the electric dipole strength given by equation (10). Consequently, we have included both J mixing by the crystal field and magnetic dipole transitions in the analysis.

5. Conclusion

Most of the discussion given here has been directed toward the derivation of even- k A_{km} such that $\rho_k A_{km}$ is a best approximation to the phenomenological B_{km} obtained from the experimental energy levels. Here the A_{km} are from the point ion model and its extension to include the dipole correction, developed at Harry Diamond Laboratories (now part of the Army Research Laboratory). We then use the theory to derive odd- k A_{km} for the electric dipole transition calculations. The derived B_{km} are used for the magnetic dipole transitions. In these calculations, the emphasis has been on predicting, rather than explaining, the quantities involved in the crystal-field splittings and the intensity of line-to-line transitions.

The research workers at Laboratoires de Bellevue, France, have extended the contributions to the quadrupole moments of the ions in the solid [111–116] obtaining $A_{km} = A_{km}^M + A_{km}^D + A_{km}^Q$. They found that the contribution from the quadrupoles, when handbook values of the dipole polarizability, α_1 , and quadrupole polarizability, α_2 , are included, is $|A_{km}^Q| < |A_{km}^D| < |A_{km}^M|$. This may be caused by saturation of both polarizabilities because of the extremely large dipole and quadrupole fields. Of course there is the possibility that the multipolar expansion diverges, but it is more likely that the handbook values of α_1 and α_2 should be considerably reduced for the calculation of A_{km}^D and A_{km}^Q . It would then seem reasonable to attempt to fit the phenomenological A_{km} as was discussed in section

2.2 by varying the point charges along with the polarizabilities. Such a procedure is very long and very tedious, and we have neither the manpower nor the funding to undertake this task.

Thus it seems that the procedure of varying the ligand charges is the method that we shall use for some time. It should not be forgotten that the purpose of varying the charges and other quantities was not just to be able to reproduce the phenomenological crystal-field parameters, B_{km} (even k), but to calculate with a certain degree of confidence the A_{km} with k odd and to use these parameters in the calculation of the transition probabilities. The so-called Judd-Ofelt parameters, which are easily calculated given the odd- k A_{km} and which are experimentally determined, differ considerably from measurement to measurement for the same ion in the same host [110]. For the heavier rare-earth ions, ignoring the magnetic dipole contributions puts the experimental results in doubt. Some experimental quantity or quantities are needed to give the quality of the predicted intensity when compared with the measured intensity.

Despite these difficulties, work will continue in predicting temperature-dependent line-to-line branching ratios and in predicting the behavior of more sophisticated laser systems. Of course, these systems will be compared with experiment wherever possible, and improvements in the theory will be instituted to bring the two into closer agreement. Work is in progress towards applying the calculated line-to-line transition probabilities to up-conversion and to energy exchange in such laser systems as Tm:Ho:YAG, and other rare-earth ion/host combinations.

Acknowledgments

Most of the early computer programming and a considerable amount of the theory presented here were done by our coworker, the late Nick Karayianis. Because of this and because of the use of Nick's extensive notes in the preparation of this report, we would like to dedicate this report to him. For extensive modification of the computer program and additional theory, we owe many thanks to our coworker Rich Leavitt. We wish to thank John Bruno for suggesting numerous improvements and frequently finding flaws in our arguments and giving us sound advice on improvement. We also wish to thank all of the members of the old Harry Diamond Laboratories for their cheerful give and take of information during their research on the optical and electron spin resonance properties of the various host/ion combinations under investigation.

References

1. K.W.H. Stevens, *Matrix Elements and Operator-Equivalents Connected with Magnetic Properties of Rare Earth Ions*, Proc. Phys. Soc. **65**, 209 (1952).
2. R. J. Elliot and K.W.H. Stevens, *The Magnetic Properties of Certain Rare-Earth Sulphates*, Proc. Phys. Soc. (London) **A219**, 387 (1953).
3. N. Karayianis and C. A. Morrison, *Operator-Equivalents*, Harry Diamond Laboratories, HDL-TR-1132 (June 1963), NTIS AD 412 893.
4. C. A. Morrison and N. Karayianis, *Operator-Equivalents for Ground States of Equivalent Electrons*, Harry Diamond Laboratories, HDL-TR-113 (June 1963), NTIS AD 412 947.
5. C. A. Morrison and R. T. Farrar, *Crystal Field Parameters for Triply Ionized Neodymium in Calcium Tungstate*, Harry Diamond Laboratories, HDL-TR-1265 (December 1964), NTIS AD 457 608.
6. J. S. Margolis, *The Energy Levels of Pr^{3+} in PrCl_3* , University of California, Los Angeles, Department of Physics Technical Report No. 1 (1960).
7. E. Y. Wong, *Absorption Spectra of $\text{Er}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Yb}(\text{C}_2\text{H}_5\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$* , J. Chem. Phys. **39**, 2781 (1963).
8. J. C. Eisenstein, *Spectrum of Nd^{3+} in LaCl_3* , J. Chem. Phys. **39**, 2134 (1963). Erratum: J. Chem. Phys. **40**, 2044 (1964).
9. J. C. Eisenstein, *Spectrum of Er^{3+} in LaCl_3* , J. Chem. Phys. **39**, 2128 (1963).
10. C. A. Morrison and D. E. Wortman, *Free Ion Energy Levels of Triply Ionized Thulium Including the Spin-Spin, Orbit-Orbit, and Spin-Other Orbit Interactions*, Harry Diamond Laboratories, HDL-TR-1563 (November 1971), NTIS AD 735 319.
11. D. E. Wortman, R. P. Leavitt, and C. A. Morrison, *Analysis of the Ground Configuration of Trivalent Thulium in Single Crystal Yttrium Vanadate*, Harry Diamond Laboratories, HDL-TR-1653 (December 1973), NTIS AD 776 343.
12. N. Karayianis, *Effective Spin-Orbit Hamiltonian*, J. Chem. Phys. **53**, 2460 (1970).
13. N. Karayianis and R. T. Farrar, *Spin-Orbit and Crystal Field Parameters for the Ground Term of Nd^{3+} in CaWO_4* , J. Chem. Phys. **53**, 3436 (1970).
14. D. E. Wortman, *Ground Term Energy Levels and Possible Effect on Laser Action for Er^{3+} in CaWO_4* , J. Opt. Soc. Am. **60**, 1143 (1970).
15. D. E. Wortman and D. Sanders, *Ground Term Energy Levels of Triply Ionized Holmium in Calcium Tungstate*, J. Chem. Phys. **53**, 1247 (1970).
16. D. E. Wortman, *Analysis of the Ground Term of Tb^{3+} in CaWO_4* , Phys. Rev. **175**, 488 (1968).

17. D. E. Wortman, *Optical Spectrum of Trivalent Dysprosium in Calcium Tungstate*, J. Chem. Phys. **55**, 7, 3212 (1971).
18. N. Karayianis, *Theoretical Energy Levels and g Values for the $4f$ Terms of Nd^{3+} and Er^{3+} in LiYF_4* , J. Phys. Chem. Solids **32**, 2385 (1971).
19. D. E. Wortman, *Ground Term Energy States for Nd^{3+} in LiYF_4* , J. Phys. Chem. Solids **33**, 311 (1972).
20. D. E. Wortman, *Optical Spectrum of Triply Ionized Erbium in Calcium Tungstate*, J. Chem. Phys. **54**, 314 (1971).
21. D. E. Wortman, *Ground Term of Nd^{3+} in LiYF_4* , Bull. Am. Phys. Soc. **16**, 594 (1971).
22. W. T. Carnall, P. R. Fields, and K. Rajnak, *Spectral Intensities of the Trivalent Lanthanides and Actinides in Solution. II. Pm^{3+} , Sm^{3+} , Eu^{3+} , Gd^{3+} , Tb^{3+} , Dy^{3+} , and Ho^{3+}* , J. Chem. Phys. **49**, 4412 (1968); *Electronic Energy Levels in the Trivalent Lanthanide Aquo Ions. I. Pr^{3+} , Nd^{3+} , Pm^{3+} , Sm^{3+} , Dy^{3+} , Ho^{3+} , Er^{3+} , and Tm^{3+}* , J. Chem. Phys. **49**, 4424 (1968); *Electronic Energy Levels of the Trivalent Lanthanide Aquo Ions. II. Gd^{3+}* , J. Chem. Phys. **49**, 4443 (1968); *Electronic Energy Levels of the Trivalent Lanthanide Aquo Ions. III. Tb^{3+}* , J. Chem. Phys. **49**, 4447 (1968); *Electronic Energy Levels of the Trivalent Lanthanide Aquo Ions. IV. Eu^{3+}* , J. Chem. Phys. **49**, 4450 (1968).
23. N. Karayianis, D. E. Wortman, and H. P. Jenssen, *Analysis of the Optical Spectrum of Ho^{3+} in LiYF_4* , J. Phys. Chem. Solids **37**, 675 (1976).
24. C. A. Morrison, N. Karayianis, and D. E. Wortman, *Theoretical Free-Ion Energies, Derivatives, and Reduced Matrix Elements, I. Pr^{3+} , Tm^{3+} , Nd^{3+} , and Er^{3+}* , Harry Diamond Laboratories, HDL-TR-1814 (July 1977), NTIS AD A042 557.
25. J. P. Sattler, *The X-Band Electron Paramagnetic Resonance Spectrum of Yb^{3+} in Eight Scheelite Crystals*, Ph.D. thesis, Georgetown University (1969).
26. J. P. Sattler and J. Nemerich, *Electron Paramagnetic Resonance of Yb^{3+} in Scheelite Single Crystals*, Phys. Rev. **B1**, 4249 (1970).
27. J. P. Sattler and J. Nemerich, *Unusual Electron Paramagnetic Resonance Hyperfine Spectra of Yb^{3+} in Scheelites*, Phys. Rev. **B1**, 4256 (1970).
28. J. P. Sattler and J. Nemerich, *Electron-Paramagnetic-Resonance Spectra of Nd^{3+} , Dy^{3+} , Er^{3+} , and Yb^{3+} in Lithium Yttrium Fluoride*, Phys. Rev. **B4**, 1 (1971).
29. I. N. Kurkin and L. Ya. Shenkun, *Paramagnetic Resonance of Trivalent Neodymium in a Single Crystal of PbMoO_4* , Sov. Phys. Solid State **6**, 1144 (1964).
30. J. Kirton, *Paramagnetic Resonance of Trivalent Holmium Ions in Calcium Tungstate*, Phys. Rev. **139**, 1930 (1965).

31. J. Kirton, *Paramagnetic Resonance of Trivalent Samarium Ions in Calcium Tungstate*, Phys. Lett. **16**, 209 (1965).
32. A. A. Antipin, I. N. Kurkin, L. D. Livanova, L. Z. Potvorova, and L. Ya. Shenkun, *Investigation of Paramagnetic Er^{3+} Centers in BaF_2 and SrF_2 Single Crystals*, Sov. Phys. Solid State **8**, 2130 (1967).
33. J. P. Sattler and J. Nemerich, *EPR of Yb^{3+} in Scheelite Single Crystals*, Harry Diamond Laboratories, HDL-TR-1485 (April 1970), NTIS AD 707 381.
34. C. A. Hutchinson, Jr., and E. Wong, *Paramagnetic Resonance in Rare-Earth Trichlorides*, J. Chem. Phys. **29**, 754 (1958).
35. S. M. Kulpa, *Excited State g Factors of Nd^{3+} in Calcium Tungstate*, Bull. Am. Phys. Soc. **16**, 448 (1971).
36. S. M. Kulpa, *Zeeman Fluorescence Studies of Neodymium in Calcium Tungstate*, J. Chem. Phys. **56**, 1198 (1972).
37. N. Karayianis, *The Significance of Crystal-Field Parameters for the ^4I Term of Nd^{3+} in CaWO_4* , Harry Diamond Laboratories, HDL-TR-1674 (December 1974), NTIS AD A011 251.
38. N. Karayianis, *Partial g-Sum Rule, a Tool for Interpreting Impurity Ion Spectra*, J. Chem. Phys. **55**, 3734 (1971).
39. G. Burns, *Shielding and Crystal Fields at Rare Earth Ions*, Phys. Rev. **128**, 2121 (1962).
40. M. T. Hutchins and D. K. Ray, *Investigations into the Origin of Crystalline Electric Field Effects on Rare Earths: I. Contributions from Neighboring Induced Moments*, Proc. Phys. Soc. (London) **81**, 663 (1963).
41. C. J. Lenander and E. Y. Wong, *Crystal-Field Shielding in PrCl_3* , J. Chem. Phys. **38**, 2750 (1963).
42. D. K. Ray, *Investigation into the Origin of the Crystalline Field Effects on Rare Earth Ions: II. Contributions from the Rare Earth Orbitals*, Proc. Phys. Soc. (London) **82**, 47 (1963).
43. G. Burns, *Crystal Fields at Rare Earth Ions*, J. Chem. Phys. **42**, 377 (1965).
44. A. K. Rachaudhuri and D. K. Ray, *Effect of the Ligand Charge Distribution on the Crystalline Field of Rare-Earth Ions*, Proc. Phys. Soc. **90**, 839 (1967).
45. R. E. Watson and A. J. Freeman, *Shielding and Distortion of Rare Earth Crystal Field Spectra*, Phys. Rev. **133**, A1571 (1964).
46. C. K. Jorgensen, *Orbitals in Atoms and Molecules*, Academic Press, New York (1962). See also D. Garcia and M. Faucher, J. Less-Common Metals **93** (1983), 119.
47. R. M. Sternheimer, *Nuclear Quadrupole Moments*, Phys. Rev. **84**, 244 (1951).

48. R. M. Sternheimer, *Electronic Polarizabilities of Ions from the Hartree-Fock Wave Functions*, Phys. Rev. **96**, 951 (1954).
49. R. M. Sternheimer, *Shielding and Antishielding Effects for Various Ions and Atomic Systems*, Phys. Rev. **146**, 140 (1966).
50. K. C. Das and A. K. Rachaudhuri, *Shielding of the Quadrupole Crystalline Electric Field at a Pr^{3+} Ion*, J. Phys. C **6**, 1385 (1973).
51. P. Erdős and J. H. Kang, *Electric Shielding of Pr^{3+} and Tm^{3+} Ions in Crystals*, Phys. Rev. **6**, B3393 (1972).
52. N. Karayianis and C. A. Morrison, *Rare-Earth Ion-Host Crystal Interactions. 2. Effect on Lattice Sums of Local Distortion and Comparison with Nd^{3+} Crystal Field Parameters*, Harry Diamond Laboratories, HDL-TR-1682 (January 1972), NTIS AD A011 752.
53. A. J. Freeman and R. E. Watson, *Theoretical Investigation of Some Magnetic and Spectroscopic Properties of Rare Earth Ions*, Phys. Rev. **127**, 2058 (1962).
54. M. Synek and L. Corsiglia, *Approximate Analytical Wavefunctions for Certain States of Nd^{3+}* , J. Chem. Phys. **48**, 3121 (1968).
55. P. Grossgut, *Analytical Wave Functions and Oscillator Strengths for Triply Ionized Cerium, Praseodymium, Neodymium, and Doubly Ionized Copper*, Ph.D. thesis, Texas Christian University, 1971 (Univ. Microfilms, Ann Arbor, MI), No. 72-7621.
56. A. V. Damommio, *Atomic Structure Calculations for Tm^{2+} and Tm^{3+}* , Ph.D. thesis, Texas Christian University, 1971 (Univ. Microfilms, Ann Arbor, MI), No. 72-7620.
57. J. Sugar, *Spectrum of Doubly Ionized Thulium (Tm III)*, J. Opt. Soc. Am. **60**, 454 (1970).
58. J. Sugar, *Energy Levels of Pr^{3+} in the Vapor State*, Phys. Rev. Lett., **14**, 731 (1965). See also: J. Sugar, *Analysis of the Spectrum of Triply Ionized Praseodymium (PrIV)*, J. Opt. Soc. Am. **55**, 1058 (1965).
59. C. Morrison, D. R. Mason, and C. Kikuchi, *Modified Slater Integrals for an Ion in Solid*, Phys. Lett. **A24**, 607 (1967). Also C. Morrison, *Host Dependence of the Rare-Earth Ion Energy Separation $4f^N - 4f^{N-1}nl$* , J. Chem. Phys. **72** (1980), 1001.
60. D. J. Newman, *Slater Parameter Shifts in Substituted Lanthanide Ions*, J. Phys. Chem. Solids **34**, 541 (1973).
61. J. C. Morrison, *Many-Body Calculations for the Heavy Atoms. III. Pair Correlations*, J. Phys. B: Atom, Molec. Phys. **6**, 2205 (1973).
62. W. B. Lewis, *Relativistic Calculations of $\langle r - 3 \rangle$ and Other $\langle r^n \rangle$ Parameters Encountered in Magnetic Resonance of Rare-Earth Ions and Atoms*, article in Proc.

XVIth Congress A.M.P.E.R.E., Bucharest, Romania (1-5 September 1970)
(Pub. House of the Academy of Soc. Rep. Rum., 1971).

63. N. Karayianis and C. A. Morrison, *Rare-Earth Ion-Host Lattice Interactions. 1. Point Charge Lattice Sum in Scheelites*, Harry Diamond Laboratories, HDL-TR-1648 (October 1973), NTIS AD 776 330.
64. L. Brewer, *Energies of the Electronic Configurations of the Lanthanide and Actinide Neutral Atoms*, J. Opt. Soc. Am. **61**, 1101 (1971).
65. R. P. Leavitt, C. A. Morrison, and D. E. Wortman, *Rare-Earth Ion-Host Lattice Interactions. 3. Three Parameter Theory of Crystal Fields*, Harry Diamond Laboratories, HDL-TR-1673 (June 1975), NTIS AD A017 849.
66. C. A. Morrison, *Dipolar Contributions to the Crystal Fields in Ionic Solids*, Solid State Commun. **18**, 153 (1976).
67. L. Brewer, *Energies of the Electronic Configurations of the Singly, Doubly, and Triply Ionized Lanthanides and Actinides*, J. Opt. Soc. Am. **61**, 1666 (1971).
68. B. R. Judd, *Optical Absorption Intensities of Rare-Earth Ions*, Phys. Rev. **127**, 750 (1962).
69. G. S. Ofelt, *Intensities of Crystal Spectra of Rare-Earth Ions*, J. Chem. Phys. **37**, 511 (1962).
70. J. D. Axe and P. P. Sorokin, *Divalent Rare Earth Spectra Selection Rules and Spectroscopy of $\text{SrCl}_2\text{:Sm}$* , Phys. Rev. **130**, 945 (1963).
71. C. A. Morrison, N. Karayianis, and D. E. Wortman, *Ion-Host Lattice Interactions. 4. Predicting Optical Spectra and Intensities of Lanthanides in Crystals*, Harry Diamond Laboratories, HDL-TR-1816 (June 1977), NTIS AD A042 447.
72. Several results of the Nd:YVO_4 intensity spectrum were obtained by D. E. Wortman and S. Kulpa (private communication).
73. D. E. Wortman, C. A. Morrison, and N. Karayianis, *Rare Earth Ion-Host Lattice Interactions. 5. Lanthanides in CaWO_4* , Harry Diamond Laboratories, HDL-TR-1794 (June 1977), NTIS AD A042 210.
74. D. E. Wortman, N. Karayianis, and C. A. Morrison, *Ion-Host Lattice Interactions. 6. Lanthanides in LiYF_4* , Harry Diamond Laboratories, HDL-TR-1770 (August 1976), NTIS AD A033 902.
75. N. Karayianis, D. E. Wortman, and C. A. Morrison, *Ion-Host Lattice Interactions. 7. Lanthanides in YVO_4* , Harry Diamond Laboratories, HDL-TR-1775 (August 1976), NTIS AD A040 905.
76. N. Karayianis, C. A. Morrison, and D. E. Wortman, *Ion-Host Lattice Interactions. 8. Lanthanides in YPO_4* , Harry Diamond Laboratories, HDL-TR-1776 (August 1976), NTIS AD A033 901.

77. D. E. Wortman, N. Karayianis, and C. A. Morrison, *Ion-Host Lattice Interactions. 9. Lanthanides in $YAsO_4$* , Harry Diamond Laboratories, HDL-TR-1722 (August 1976), NTIS AD A030 658.
78. C. A. Morrison, N. Karayianis, and D. E. Wortman, *Ion-Host Lattice Interactions. 10. Lanthanides in $Y_2SiBe_2O_7$* , Harry Diamond Laboratories, HDL-TR-1766 (August 1976), NTIS AD A030 849.
79. D. E. Wortman, C. A. Morrison, and N. Karayianis, *Ion-Host Lattice Interactions. 11. Lanthanides in $Y_3Al_5O_{12}$* , Harry Diamond Laboratories, HDL-TR-1773 (August 1976), NTIS AD A033 884.
80. N. Karayianis, D. E. Wortman, and C. A. Morrison, *Ion-Host Lattice Interactions. 12. Lanthanides in $Y_3Ga_5O_{12}$* , Harry Diamond Laboratories, HDL-TR-1793 (July 1977), NTIS AD A042 205.
81. C. A. Morrison, N. Karayianis, and D. E. Wortman, *Ion-Host Lattice Interactions. 13. Lanthanides in $YAlO_3$* , Harry Diamond Laboratories, HDL-TR-1788 (February 1977), NTIS AD A038 050.
82. C. A. Morrison, D. E. Wortman, and N. Karayianis, *Ion-Host Lattice Interactions. 14. Lanthanides in LnP_5O_{14}* , Harry Diamond Laboratories, HDL-TR-1779 (February 1977), NTIS AD A037 179.
83. R. P. Leavitt and C. A. Morrison, *Crystal-Field Analysis of Triply Ionized Rare Earth Ions in Lanthanum Trifluoride. II. Intensity Calculations*, J. Chem. Phys. **73**, 749 (1980). The computation results are contained in the AIP document no. PAPS-JCPSA-73-749-401, containing 401 pages of transition probability calculations. A description of the contents of this supplement is given in the paper.
84. M. E. Rose, *Elementary Theory of Angular Momentum*, Wiley (1957).
85. See reference 71 and references therein.
86. C. A. Morrison and R. P. Leavitt, *Crystal Field Analysis of Triply Ionized Rare Earth Ions in Lanthanum Trifluoride*, J. Chem. Phys. **71**, 2366 (1979).
87. N. C. Chang, J. B. Gruber, R. P. Leavitt, and C. A. Morrison, *Optical Spectra, Energy Levels, and Crystal-Field Analysis of Tripositive Rare Earth Ions in Y_2O_3 . I. Kramers Ions in C_2 Sites*, J. Chem. Phys. **76**, 3877 (1982).
88. R. P. Leavitt, J. B. Gruber, N. C. Chang, and C. A. Morrison, *Optical Spectra, Energy Levels, and Crystal-Field Analysis of Tripositive Rare Earth Ions in Y_2O_3 . II. Non-Kramer Ions in C_2 Sites*, J. Chem. Phys. **76**, 4775 (1982).
89. C. A. Morrison, R. P. Leavitt, J. B. Gruber, and N. C. Chang, *Optical Spectra, Energy Levels, and Crystal-Field Analysis of Tripositive Rare Earth Ions in Y_2O_3 . III. Intensities and g Values for C_2 Sites*, J. Chem. Phys. **79**, 4758 (1983).
90. J. B. Gruber, R. P. Leavitt, C. A. Morrison, and N. C. Chang, *Optical Spectra, Energy Levels, and Crystal-Field Analysis of Tripositive Rare Earth Ions in Y_2O_3 . IV. C_{3i} Sites*, J. Chem. Phys. **82**, 5373 (1985).

91. C. A. Morrison and R. P. Leavitt, *Crystal Field Analysis of Nd³⁺ and Er³⁺ in Bi₄Ge₃O₁₂*, J. Chem. Phys. **74**, 25 (1981).
92. J. B. Gruber, M. E. Hills, M. P. Nadler, M. R. Kokta, and C. A. Morrison, *Absorption Spectra and Energy Levels of Sm³⁺:Y₃Al₅O₁₂*, Chem. Phys. **113**, 175 (1987).
93. J. B. Gruber, M. E. Hills, R. M. Macfarlane, C. A. Morrison, and G. A. Turner, *Symmetry, Selection Rules, and Energy Levels of Pr³⁺:Y₃Al₅O₁₂*, Chem. Phys. **134**, 241 (1989).
94. J. B. Gruber, M. E. Hills, R. M. Macfarlane, C. A. Morrison, G. A. Turner, G. J. Quarles, G. J. Kintz, and L. Esterowitz, *Spectra and Energy Levels of Tm³⁺:Y₃Al₅O₁₂*, Phys. Rev. **B40**, 9464 (1989).
95. S. B. Stevens, C. A. Morrison, M. D. Seltzer, M. E. Hills, and J. B. Gruber, *Emission Measurements and Crystal-Field Calculations for ⁴G_{5/2} to ⁶H_{7/2} Transitions in Sm³⁺:YAG*, J. Appl. Phys. **70**, 948 (1991).
96. J. B. Gruber, M. E. Hills, M. D. Seltzer, S. B. Stevens, and C. A. Morrison, *Analysis of the Spectrum of Trivalent Holmium in Yttrium Scandium Gallium Garnet*, J. Appl. Phys. **72**, 5253 (1992).
97. J. B. Gruber, M. E. Hills, C. A. Morrison, G. A. Turner, and M. R. Kokta, *Absorption Spectra and Energy Levels of Gd³⁺, Nd³⁺, and Cr³⁺ in the Garnet Gd₃Sc₂Ga₃O₁₂*, Phys. Rev. **B37**, 8564 (1988).
98. T. Allik, S. Stewart, D. Sardar, G. Quarles, R. Powell, C. Morrison, G. Turner, M. Kokta, W. Hovis, and A. Pinto, *Preparation, Structures, and Spectroscopic Properties of Nd³⁺:(La_{1-x}Lu_x)₃(Lu_{1-y}Ga_y)Ga₃O₁₂ Crystals*, Phys. Rev. **B37**, 9129 (1988).
99. T. H. Allik, C. A. Morrison, J. B. Gruber, and M. R. Kokta, *Crystallography, Spectroscopic Analysis, and Lasing Properties of Nd³⁺:Y₃Sc₂Al₃O₁₂*, Phys. Rev. **B41**, 21 (1990).
100. J. B. Gruber, M. E. Hills, M. D. Seltzer, G. A. Turner, C. A. Morrison, and M. R. Kokta, *Spectroscopic Analysis of Er³⁺ (4f¹¹) in Y₃Sc₂Al₃O₁₂*, Chem. Phys. **144**, 342 (1990).
101. J. B. Gruber, M. D. Seltzer, M. E. Hills, S. B. Stevens, and C. A. Morrison, *Energy Levels and Upconversion Fluorescence in Trivalent Thulium-Doped Yttrium Scandium Aluminum Garnet*, J. Appl. Phys. **73**, 1929 (1993).
102. C. A. Morrison and D. E. Wortman, *Energy Levels of Rare-Earth Ions in Rare-Earth Arsenides*, Opt. Mater. **1**, 195 (1992).
103. J. Schneider, H. D. Müller, J. D. Ralston, F. Fuchs, A. Dörnen, and K. Thonke, *Crystal-Field Splittings of Er³⁺ (4f¹¹) in Molecular Beam Epitaxially Grown ErAs/GaAs*, Appl. Phys. Lett. **59**, 34 (1991).

104. D. E. Wortman and C. A. Morrison, *Energy Levels and Predicted Absorption Spectra of Rare-Earth Ions in Rare-Earth Arsenides*, Harry Diamond Laboratories, HDL-TM-92-25 (November 1992), NTIS AD A259 136.
105. E. D. Filer, C. A. Morrison, G. A. Turner, and N. Barnes, *Theoretical Branch Ratios for the 5I_7 to 5I_8 Levels of Ho^{3+} in the Garnets $A_3B_2C_3O_{12}$ ($A = Y, La, Lu, Gd$; $B = Al, Lu, Sc, Ga$; $C = Al, Ga$)*, OSA Proc. Advanced Solid State Lasers **6**, 354 (1991).
106. E. D. Filer, N. P. Barnes, and C. A. Morrison, *Theoretical Temperature-Dependent Branching Ratios and Laser Thresholds of the 3F_4 to 3H_6 Levels to Tm^{3+} in Ten Garnets*, OSA Proc. Advanced Solid State Lasers **10**, 189 (1991).
107. N. Karayianis, C. A. Morrison, and D. E. Wortman, *Crystal Field Parameters for the Pentaphosphates of Neodymium and Europium*, J. Chem. Phys. **64**, 3890 (1976).
108. R. P. Leavitt, *On the Role of Certain Rotational Invariants in Crystal-Field Theory*, J. Chem. Phys. **77**, 1661 (1982).
109. F. Auzel, *L'Auto-extinction de Nd^{3+} : Son mécanisme fondamental et un critère prédictif simple pour les matériaux minilaser*, Nat. Res. Bull. **14**, 223 (1975).
110. C. A. Morrison and R. P. Leavitt, *Spectroscopic Properties of Triply Ionized Lanthanides in Transparent Host Materials*, in Volume 5, *Handbook of the Physics and Chemistry of Rare Earths*, ed. by K. A. Gschneidner, Jr., and L. Eyring, North-Holland publishers, New York, NY (1982).
111. M. Faucher and D. Garcia, *Electrostatic Crystal-Field Contributions in Rare Earth Compounds with Consistent Multipolar Effects: I. Contribution to k-Even Parameters*, Phys. Rev. **B26**, 5451 (1982).
112. D. Garcia, M. Faucher, and O. L. Malta, *Electrostatic Crystal-Field Contributions in Rare-Earth Compounds with Consistent Multipolar Effects: II. Contributions to K-Odd Parameters (Transition Probabilities)*, Phys. Rev. **B27**, 7386 (1983).
113. D. Garcia and M. Faucher, *Crystal-Field Parameters in Rare-Earth Compounds: Extended Charge Contributions*, Phys. Rev. **A30**, 1703 (1984).
114. D. Garcia, *Simulation ab initio des parametres du champ des ligandes*, Thesis, L'Ecole Centrale des Arts et Manufactures (27 Juin 1983).
115. M. Faucher and P. Caro, *A Quickly Converging Method for Computing Electrostatic Crystal-Field Parameters*, J. Chem. Phys. **66**, 1273 (1977).
116. M. Faucher and D. Garcia, *Crystal Field Effects on 4f Electrons: Theories and Reality*, J. Less-Common Metals **93**, 31 (1983).

Distribution

Admnstr
Defns Techl Info Ctr
Attn DTIC-DDA (2 copies)
Cameron Sta Bldg 5
Alexandria VA 22304-6145

Defns Advncd Rsrch Proj Agcy
Attn A Yang
1400 Wilson Blvd
Arlington VA 22290

Director
Defns Nuc Agcy
Attn TITL Tech Lib
6801 Telegraph Rd
Alexandria VA 22310-3398

Ofc of the Dpty Chief of Staf for Rsrch Dev &
Acqstn
Attn DAMA-ARZ-B I R Hershner
Dept of the Army
Washington DC 20310

Under Secy of Defns Rsrch & Engrg
Attn Techl Lib 3C128
Washington DC 20301

Commander
Atmospheric Sci Lab
Attn Techl Lib
White Sands Missile Range NM 88002-5030

Director
Night Vsn & Electro-Optics Lab
Attn A Pinto (2 copies)
Attn B Zandi
Attn J Daunt
Attn L Merkel
Attn R Buser
Attn J A Hutchinson
Attn Techl Lib
Attn W Tressel
FT Belvoir VA 22060

Commander
US Army Mis & Munitions Ctr & Schl
Attn AMSMI-TB Redstone Sci Info Ctr
Attn ATSK-CTD-F
Redstone Arsenal AL 35809

US Army Mtrl & Mech Rsrch Ctr
Attn SLCMT-TL Techl Lib
Watertown MA 02172

US Army Rsrch Ofc
Attn G Iafrate
Attn M Strosio
Attn M Ciftan
Attn R Guenther
PO Box 12211
Research Triangle Park NJ 07709-2211

US Army Test & Eval Cmnd
Attn D H Sliney
Attn Techl Lib
Aberdeen Proving Ground MD 21005

US Army Troop Spprt Cmnd
Attn STRNC-RTL Techl Lib
Natick MA 01762

Commanding Officer
US Frgn Sci & Techlgy Ctr
Attn AIAST-BS Basic Sci Div
Federal Office Building
Charlottesville VA 22901

Director
Nav Rsrch Lab
Attn A Rosenbaum
Attn Code 2620 Tech Lib Br
Attn Code 5554 F Bartoli
Attn Code 5554 L Esterowitz
Attn Code 5554 R E Allen
Attn G Quarles
Attn G Risenblatt
Washington DC 20375

Distribution

Commander
Nav Weapons Ctr
Attn A Wright
Attn M D Seltzer
Attn D C Harris
Attn Code 3854 M Nader
Attn Code 3854 R L Atkins
Attn DOCE343 Techl Info Dept
China Lake CA 93555

Ames Lab Dow Iowa State Univ
Attn K A Gschneidner Jr
Ames IA 50011

Argonne Natl Lab
Attn W T Carnall
9700 South Cass Ave
Argonne IL 60439

Director
Lawrence Radiation Lab
Attn L D DeLoach
Attn S A Payne
Attn M J Weber
Attn W Krupke
Livermore CA 94550

Los Alamos Natl Lab
Attn E T Salesky
505 Openheimer Dr
Los Alamos NM 87544

Oak Ridge Natl Lab
Attn R G Haire
Oak Ridge TN 37839

NASA Langley Rsrch Ctr
Attn C Blair
Attn D Getteny
Attn G Armagen
Attn J Barnes
Attn M Buoncristiani
Attn N P Barnes (2 copies)
Attn P Cross
Hampton VA 23665

Natl Inst of Stand & Techlgy
Attn Lib
Gaithersburg MD 20899

Natl Oceanic & Atmospheric Adm Envir
Rsrch Lab
Attn Lib R-51 Techl Rpt
Boulder CO 80302

Arizona State Univ Dept of Chemistry
Attn L Eyring
Tempe AZ 85281

Colorado State Univ Physics Dept
Attn S Kern
FT Collins CO 80523

Deptmento De Química Fundamental &
Deptmento de Fisica
Attn A da Gama
Attn G F de Sá
Attn O L Malta
da UFPE Cidade Universitaria
50,000 Recife Pe
Brasil

Howard Univ Dept of Physics
Attn Prof V Kushamaha
25 Bryant Stret NW
Washington DC 20059

Johns Hopkins Univ Dept of Physics
Attn B R Judd
Baltimore MD 21218

Kalamazoo Colg Dept of Physics
Attn K Rajnak
Kalamazoo MI 49007

MA Inst of Techlgy Crystal Physics Lab
Attn H P Jenssen
Cambridge MA 02139

Princeton Univ Dept of Chemistry
Attn C Weaver
Attn D S McClure
Princeton NJ 08544

Distribution

San Jose State Univ Dept of Physics
Attn J B Gruber
San Jose CA 95192

Seton Hall Univ Chemistry Dept
Attn H Brittain
South Orange NJ 07099

Univ of Central Florida Dept of Physics
Attn B H T Chai
Attn R E Peale
Orlando FL 32816

Univ of Connecticut Dept of Physics
Attn R H Bartram
Storrs CT 06269

Univ of Dayton Dept of Physics
Attn S P Sinha
300 College Park
Dayton OH 45469-2350

Univ of Illinois Everitt Lab
Attn J G Eden
1406 W Green Stret
Urbana IL 61801

Univ of Michigan Dept of Physics
Attn S C Rand
Ann Arbor MI 48109

Univ of Minnesota Duluth Dept of
Chemistry
Attn L C Thompson
Duluth MN 55812

Univ of South Florida Physics Dept
Attn R Chang
Attn Sengupta
Tampa FL 33620

Univ of Southern California
Attn M Birnbaum
Los Angeles CA 90089

Univ of Virginia Dept of Chemistry
Attn F S Richardson
Charlottesville VA 22901

Univ of Wisconsin Chemistry Dept
Attn J Wright
Madison WI 53706

Université Claude Bernard
Attn R Moncorgé
43 boulevard du 11 Novembre 1918
69622 Villeurbanne
France

UPR 210 CNRS
Attn M Faucher
Attn P Caro
Attn P Porcher
1 Place A Briand 92195
Meudon Cedex

Allied Signal Inc
Attn R Morris
POB 1021 R
Morristown NJ 07960

Arspec Corp
Attn N C Chang
PO Box 92957
Los Angeles CA 90009

Battelle Pac Northwest Lab Battelle Blvd
Attn N Hess
PO Box 999
Richland WA 99352

Dept of Mech Indus & Arspec Eng
Attn S Temkin
PO Box 909
Piscataway NJ 08854

Engrg Societies Lib
Attn Acqstn Dept
345 East 47th Stret
New York NY 10017

Fibertech Inc
Attn H R Verdin
510-A Herdon Pky
Herdon VA 22070

Distribution

Hughes Aircraft Comp
Attn D Sumida
Attn MS RL65 R A McFarlane
3011 Malibu Canyon Rd
Malibu CA 90265

IBM Rsrch Div Almaden Rsrch Ctr
Attn R M Macfarlane Mail Stop K32 802(d)
650 Harry Rd
San Jose CA 95120

Inst for Low Temp & Struc Rsrch Polish
Academy of Sci
Attn R Troc
50-950 Wroclaw PO Box 937
ul. Okolna 2
Poland

Lawrence Berkeley Lab
Attn N Edelstein
MS 70A-1150
Berkeley CA 94720

LTV
Attn M Kock (WT-50)
PO Box 650003
Dallas TX 75265

Martin Marietta
Attn F Crowne
Attn J Little
Attn P Caldwell
Attn T Worchesky
1450 South Rolling Rd
Baltimore MD 21227

McDonnell Douglass Elect Sys Comp
Attn Dept Y440 Bldg 101 Lev 2Rm/PTB54 D
M Andrauskas MS-2066267
PO Box 516
ST Louis MO 63166

MIT Lincoln Lab
Attn B Aull
PO Box 73
Lexington MA 02173

Montana Analytic Services
Attn M Schwan
325 Icepond Rd
Bozeman MT 59715

Sci Applctn Intrntl Corp
Attn T Allik
1710 Goodridge Dr
McLean VA 22102

Southwest Rsrch Inst
Attn M J Sablik
PO Drawer 28510
San Antonio TX 78228-0510

Swartz Electro-Optic Inc
Attn G A Rines
45 Winthrop Stret
Concord MA 01742

Union Carbide Corp
Attn M R Kokta
50 South 32nd Stret
Washougal WA 98671

Univ of Toronto Dept of Physics
Attn D May
Toronto Ontario MSS1A7
Canada

W J Schafer Assoc
Attn J W Collins
321 Ballerica Rd
Chelmsford MA 01824

Distribution

US Army Rsrch Lab

Attn AMSRL-EP C Thornton

Attn AMSRL-EP M Thompsett

Attn AMSRL-EP-C T Aucoin

FT Monmouth NJ 07703-5601

U.S. Army Rsrch Lab

Attn AMSRL-OP-SD-TA Mail & Records
Mgmt

Attn AMSRL-OP-SD-TL Tech Library
(3 copies)

Attn AMSRL-OP-SD-TP Tech Pub

Attn AMSRL-PS-AA C Morrison

Attn AMSRL-PS-AA D Wortman

Attn AMSRL-PS-AA G Simonis

Attn AMSRL-PS-AA J Bradshaw

Attn AMSRL-PS-AA J Bruno

Attn AMSRL-PS-AA J Pham

US Army Rsrch Lab (cont'd)

Attn AMSRL-PS-AA M Stead

Attn AMSRL-PS-AA M Tobin

Attn AMSRL-PS-AA R Leavitt

Attn AMSRL-PS-AA R Tober

Attn AMSRL-PS-AA T Bahder

Attn AMSRL-SE-EO C Garvin

Attn AMSRL-SE-EO J Goff

Attn AMSRL-SE-EP J Nemarich

Attn AMSRL-SE-RM (A) Chf

Attn AMSRL-SE-RU A Bencivenga

Attn AMSRL-SE-RU B Zabudowski

Attn AMSRL-SS-FA G Turner

Attn AMSRL-WT Chf Scentst

Attn AMSRL-WT-NG B McLean

Attn AMSRL-WT-NG Chf

Adelphi MD 20783-1197